

## EFFECT OF DOPING IN THE Bi-Sr-Ca-Cu-O SUPERCONDUCTOR

S. A. Akbar, M. S. Wong, M. J. Botelho, and Y. M. Sung  
 Department of Materials Science and Engineering  
 The Ohio State University  
 Columbus, OH 43210

and

M. Alauddin, C. E. Drummer, and M. J. Fair  
 Department of Chemistry  
 Wagner College  
 Staten Island, NY 10301

*Abstract*

The results of the effect of doping on the superconducting transition in the Bi-Sr-Ca-Cu-O system are reported. Samples were prepared under identical conditions with varying types (Pb, Sb, Sn, Nb) and amounts of dopants. All samples consisted of multiple phases, and showed stable and reproducible superconducting transitions. Stabilization of the well known 110 K phase depends on both the type and amount of dopant. No trace of superconducting phase of 150 K and above was observed.

**I. Introduction**

Superconductivity in the Bi-Sr-Ca-Cu-O system was originally reported by Michel et al. [1] and later by Maeda et al. [2] and Chu et al. [3]. There exists three distinct superconducting phases [1-7] in this system, the orthorhombic unit cell structures of which differ [8] in the number of Cu-O planes ( $n$ ). The nominal compositions of these phases are: (i)  $\text{Bi}_2\text{Sr}_2\text{CuO}_4$  ( $n=1$ ,  $T_c < 20\text{K}$ ; 2201 phase), (ii)  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$  ( $n=2$ ,  $T_c = 85\text{K}$ ; 2212 phase) and (iii)  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$  ( $n=3$ ,  $T_c = 110\text{K}$ ; 2223 phase). It has been quite difficult to synthesize the 110K phase, the formation of which has been reported to be enhanced by Pb doping [9-16].

Recently, Hongbao et al. [17-19] reported even higher transition temperatures (as high as 164K) in the Bi-Pb-Sb-Sr-Ca-Cu-O system. They, however, reported significant instability of the high-temperature superconducting phase. Their data show large drops in  $T_c$  values after the samples are circled from liquid nitrogen to room temperature in air. This prompted us to do a systematic study of the effect of doping on superconductivity in these systems, and the results are communicated in this paper. Since our objective was to investigate the effect of doping, all the samples in this study were prepared under the same processing condition. The effect of variation in processing conditions is under investigation and will be reported in a future communication.

**II. Experimental**

The samples were prepared by the standard solid state reaction route by mixing  $\text{Bi}_2\text{O}_3$ ,  $\text{PbO}$ ,  $\text{Sb}_2\text{O}_3$  ( $\text{Sb}_2\text{S}_3$  for sample #12),  $\text{SnO}$  (for #13),  $\text{Nb}_2\text{O}_5$  (for #14),  $\text{SrCO}_3$ ,  $\text{CaCO}_3$ , and  $\text{CuO}$  in stoichiometric ratios. All of the starting materials were dried in oven at  $160^\circ\text{C}$  for an hour and stored in desicator prior to weighing. This is clearly preferable to weighing the raw materials "as is" since a recent report (20) indicates that many oxides contain variable amount of hydroxides which may affect the composition of the final product. The mixtures were calcined at  $820^\circ\text{C}$  for 12 hrs. After grinding and

pressing into disk-shaped pellets, the samples were then sintered in air at 860 °C for 60 hrs. followed by a fast cool (10 °C/min.). The nominal compositions of the samples prepared are given in Table I.

Table I: Summary of properties of the samples investigated

No.	Composition*	Processing Conditions	$T_{c,zero}$ (K)
1	2-0-0-0-0-2-2-3-y-0	calcined at 820 °C for 12 hrs. and sintered at 860 °C for 60 hrs.	80
2	1.7-.25-.05-0-0-2-2-3-y-0	"	94
3	1.7-.2-.1-0-0-2-2-3-y-0	"	107
4	1.7-.15-.15-0-0-2-2-3-y-0	"	100
5	1.6-.3-.1-0-0-2-2-3-y-0	"	106
6	1.7-.2-.1-0-0-2-2-3.4-y-0	"	95
7	1.6-.2-.2-0-0-2-2-3-y-0	"	82
8	1.7-.2-.1-0-0-2-2-2.6-y-0	"	<70
9	1.5-.4-.1-0-0-2-2-3-y-0	"	99
10	1.5-.5-0-0-0-2-2-3-y-0	"	90
11	1.7-.3-0-0-0-2-2-3-y-0	"	<70
12	1.7-.2-.1-0-0-2-2-3-y-z	"	81
13	1.7-0-.1-0-.2-2-2-3.6-y-0	"	72
14	1.5-.2-.1-.2-0-2-2-3-y-0	"	107

\*Numbers represent p, q, r, s, u, v, w and x in  $Bi_pPb_qSb_rNb_sSn_uSr_vCa_wCu_xO_yS_z$

Resistance vs. temperature measurements were performed by the standard four-probe ac method with a PAR lock-in amplifier. The X-ray powder diffraction (XRD) patterns were taken on a Philips diffractometer at room temperature. The microstructural pictures were taken on an ISI-SX-40 scanning electron microscope (SEM). The ac magnetic susceptibility measurements were performed using a recently developed system by Xenikos et al. (21). This system detects the variation in the inductance of a coil which is induced when the sample changes its magnetic behavior. This variation causes change in the resonant frequency of the coil which corresponds to a change in the output voltage. The data is therefore conveniently represented in terms of detector output voltage as a function of temperature.

### III. Results and Discussions

Most of our samples, with the exception of a few, exhibited superconductivity. The pure 2223-sample (#1) showed a very broad transition (Fig.1a) with a low  $T_c$  (~80 K). The doped samples, on the other hand, showed sharp transition with higher  $T_c$  ~107 K (a plot is shown in Fig.1b for sample #3). The  $T_c$  values reported in this paper represent the temperatures at which the resistance of the samples

goes to zero. It is interesting to note that none of our samples showed significant hysteresis in  $R$  vs.  $T$  behavior with temperature cycles as reported by Hongbao et al. [18,19]. This indicates that we were able to make rather stable and reproducible samples. We were, however, unable to make any sample showing  $T_C$  values as high as reported by Hongbao et al. We prepared one sample (#12) with similar nominal

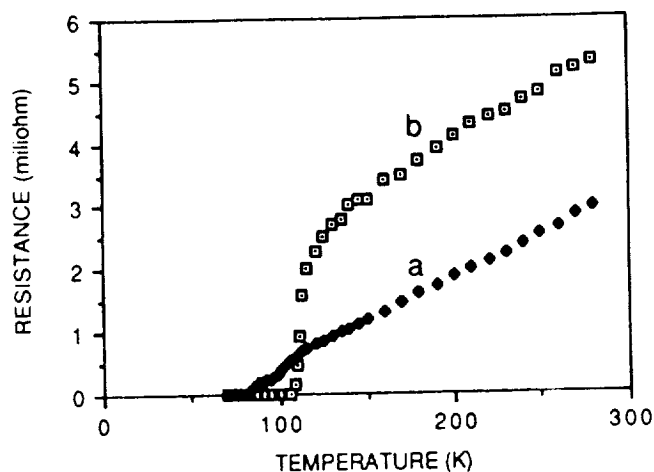


Fig.1 Resistance vs. temperature of sample #1 (a) and sample #3 (b).

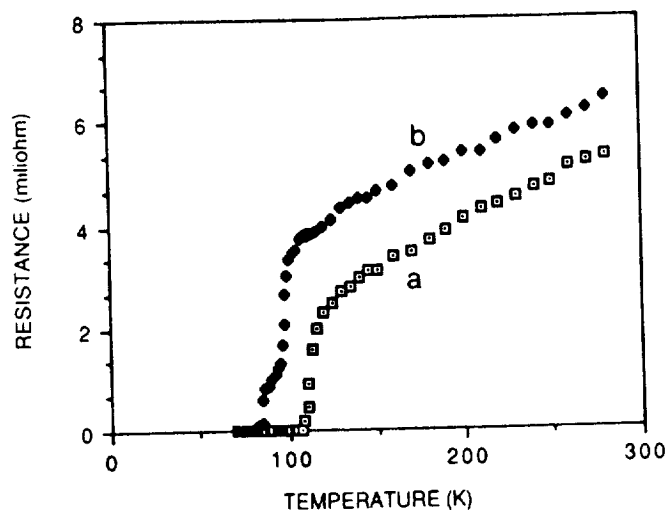


Fig.2 Resistance vs. temperature of sample #3 (a) and sample #12 (b)

composition as that of sample #2, but with different oxygen stoichiometry ( $Sb_2S_3$  was used instead of  $Sb_2O_3$ ). And our data (Fig.2a; #3 and Fig.2b; #12) indicates that the use of sulfide dopants instead of oxides is detrimental to superconductivity in this system. Also a Sn-doped sample shows a lower  $T_C$  than a corresponding Pb-doped sample (Fig.3). On the other hand, both Nb and Pb doping seem to stabilize the well known 110 K phase (Fig.4). The superconducting transitions in our samples were also confirmed by the ac magnetic susceptibility measurements. Figure 5 shows susceptibility data for samples #1(a) and #3(b).

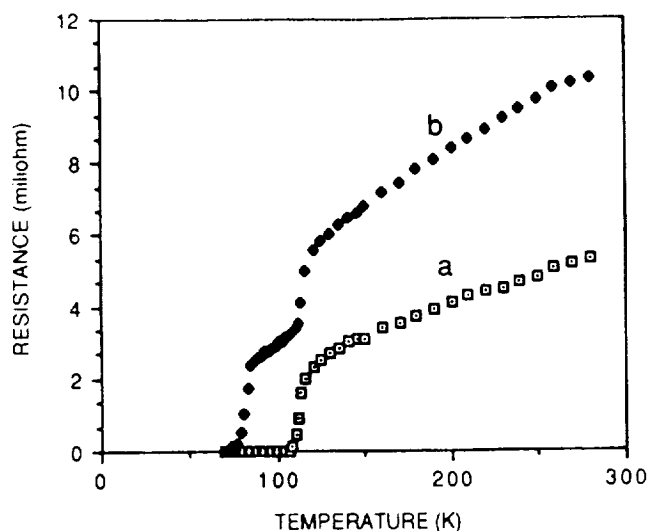


Fig.3 Resistance vs. temperature of sample #3 (a) and sample #13 (b).

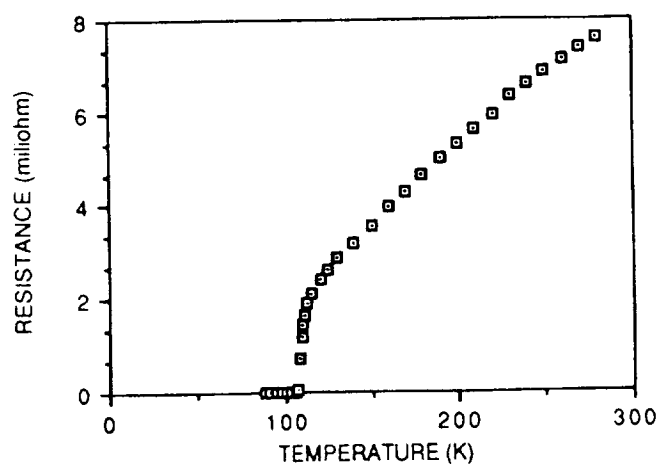


Fig.4 Resistance vs. temperature of a Pb and Nb-doped sample (#14)

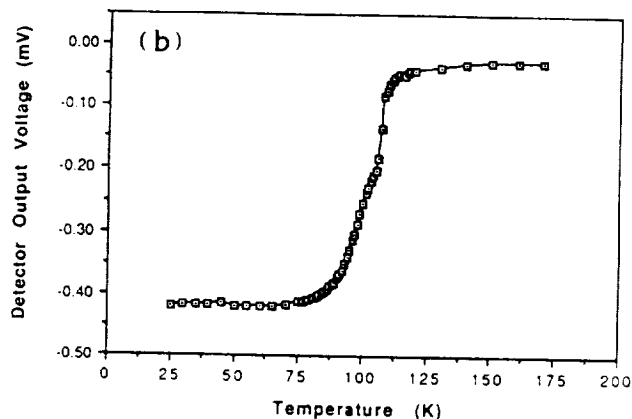
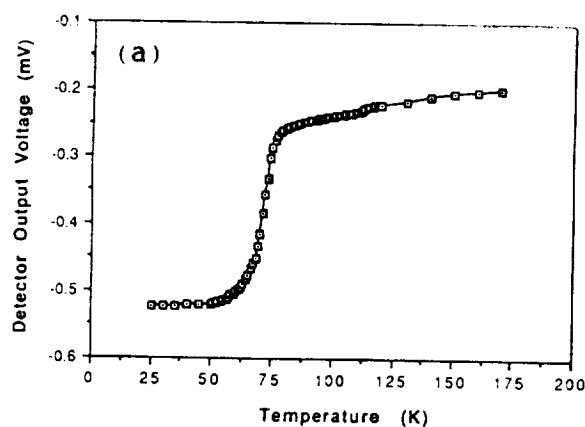


Fig.5 The ac magnetic susceptibility data of samples #1 (a) and #3 (b).  
The zero of the voltage scale is arbitrary.

The X-ray diffraction data of samples #1, 2, 3 and 4 are shown in Fig.6, which compare very well with those reported in the literature. It is quite evident that our samples constituted mostly of 2223 and 2212 phases and some 2201 phase. It is also interesting to note that as the amount of Sb

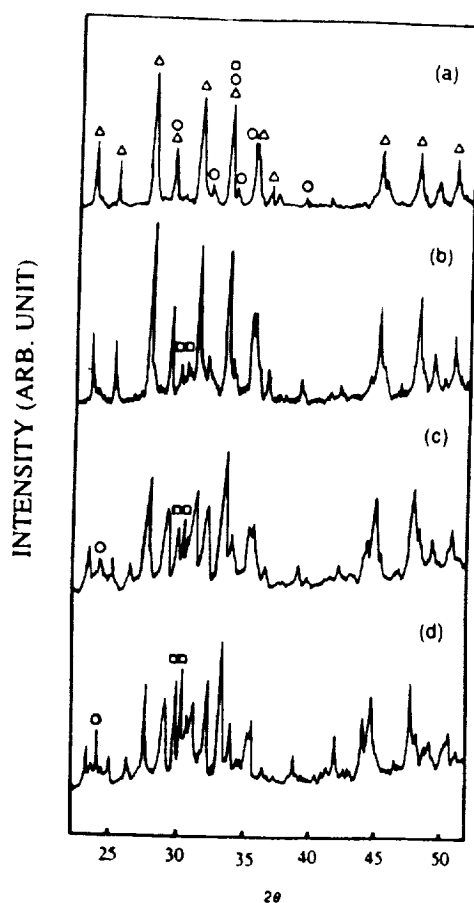


Fig.6 X-ray diffraction of samples #1 (a),  
#2 (b), #3 (c) and #4 (d).  
□ 2201, Δ 2212 and ○ 2223.

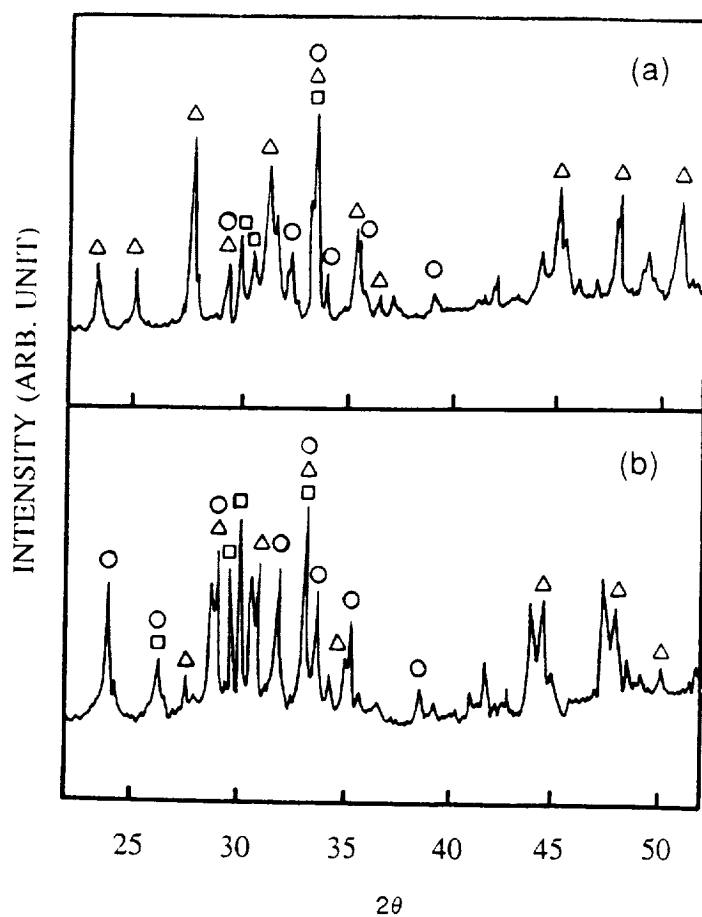


Fig.7 X-ray diffraction of samples #13  
(a) and #14 (b).

increases from sample #1 to #2 to #3 to #4, two diffraction peaks around  $30^\circ$  become more and more dominant. The XRD patterns of the Sn and Nb-doped samples (Fig.7) indicate that they are also multiphase, consisting of mostly 2223 and 2212 peaks.

Figure 8 shows SEM micrographs of sample #3 (a: as prepared surface, b: fractured surface) revealing plate-like grains, a characteristic of all the samples including the Sn and Nb-doped samples. None of the micrographs of our samples showed any indication of thin filaments which were claimed to be responsible for superconductivity above 150K in the work of Hongbao et al. [19].

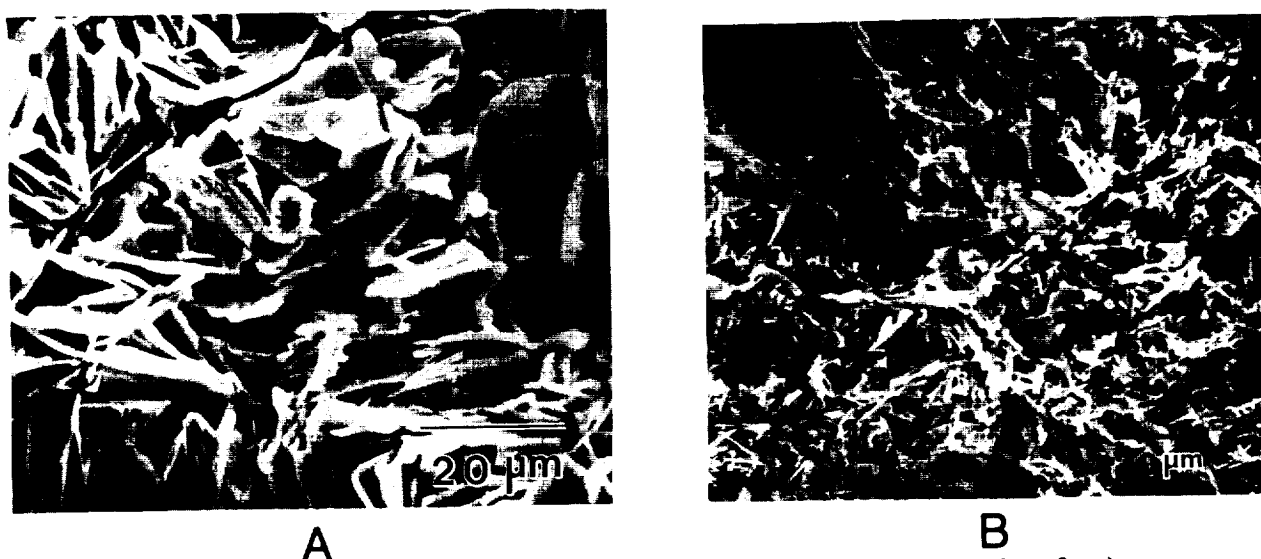


Fig.8 SEM micrograph of sample #3 (a: as prepared surface, b: fractured surface).

This study was not able to reproduce any of the superconducting phase above 150 K as reported by Hongbao et al. [19] in the Bi-Pb-Sb-Sr-Ca-Cu-O system. In the composition range of Pb and Sb doping we studied, the optimum nominal composition for the well known 110 K phase is that of sample #3. Doping the material with both Pb and Nb seem to stabilize the 110 K phase. Based on the XRD and SEM data, it is not possible to highlight any particularly distinguishing features of the Sn and Nb-doped samples from their Pb-doped counterpart.

#### IV. References

1. C. Michel, M. Herrien, M. M. Borel, A. Grandin, F. Deslandes, J. Provost and B. Raveau, *Z. Phys.*, **B68**, 421 (1987).
2. M. Maeda, Y. Tanaka, M. Fukutomi and T. Asano, *Jpn J. Appl. Phys. Lett.*, **27**, L209 (1988).
3. C. W. Chu, J. Bechtold, L. Gao, P. H. Hor, Z. J. Huang, R. L. Meng, Y. Y. Sun, Y. Q. Wang and Y. Y. Xue, *Phys. Rev. Lett.*, **60**, 941 (1988).
4. S. S. P. Parkin, V. Y. Lee, A. I. Nazzal, R. Savoy, R. Beyers and S. J. Laplaca, *Phys. Rev. Lett.*, **61**, 750 (1988).
5. M. A. Subramanian, C. C. Torardi, J. C. Calabrese, J. Gopalakrishnan, K. J. Morrissey, T. R. Askew, R. B. Flippen, U. Chowdhury and A. W. Sleight, *Science*, **239**, 1015 (1988).

6. H. W. Zandbergen, Y. K. Huang, M. J. V. Menken, J. N. Li, K. Kadowaki, A. A. Menovsky, G. Van Tendeloo and S. Amelinckx, *Nature*, **333**, 620 (1988).
7. R. M. Hazen, C. T. Prewitt, R. G. Angel, N. L. Roy, L. W. Finger, C. G. Hadidiacos, D. R. Veblen, P. J. Heaney, P. H. Hor, R. L. Meng, Y. Y. Sun, Y. Q. Wang, Y. Y. Xua, Z. J. Huang, L. Gao, J. Bechtold and C. W. Chu, *Phys. Rev. Lett.*, **60**, 1174 (1988).
8. D. Shi, M. Tang, K. Vandervoort and H. Claus, *Phys. Rev.* **B39**, 9091 (1989).
9. U. Balachandran, D. Shi, D. I. Dos Santos, S. W. Graham, M. A. Patel, B. Tani, K. Vandervoort, H. Claus and R. B. Poeppel, *Physica C* **156**, 649 (1988).
10. T. Kanai, T. Kumagai, A. Soeta, T. Suzuki, K. Aiharaa, T. Kamo and S. Matsuda, *Jpn. J. Appl. Phys.*, **27**, L1435 (1988).
11. T. Hatano, K. Aota, S. Ikeda, K. Nakamura and K. Ogawa, *Jpn. J. Appl. Phys.*, **27**, L2055 (1988).
12. T. Komatsu, R. Sato, K. Matusita and Y. Yamashita, *Appl. Phys. Lett.*, **54**, 1170 (1989).
13. S. M. Green, C. Jiang, Y. Mei, H. L. Luo and C. Politis, *Phys. Rev.*, **B38**, 5016 (1988).
14. S. M. Green, Y. Mei, A. E. Manzi, H. L. Luo, R. Ramesh and G. Thomas, *J. Appl. Phys.*, **66**, 728 (1989).
15. Y. Mei, S. M. Green, C. Jiang and H. L. Luo, *J. Appl. Phys.*, **66**, 1777 (1989).
16. D. Shi, M. S. Boley, J. G. Chen, M. Xu, K. Vandervoort, Y. X. Liao, A. Zangvil, J. Akujieze and C. Segre, *Appl. Phys. Lett.*, **55**, 699 (1989).
17. L. Hongbao, Z. Xiaonxong, C. Yaogu, Z. Guien, R. Yaozhong, C. Zhaojia and Z. Yuheng, *Physica C*, **156**, 804 (1988).
18. L. Hongbao, C. Liezhao, Z. Ling, M. Zhiqiang, Z. Weijie, L. Xiaoxian, Y. Zhidong, X. Bai, M. Xianglei, Z. Guein, R. Yaozhong, C. Zhaojia, and Z. Yuheng, *Solid State Commun.*, **69**, 867 (1989).
19. L. Hongbao, C. Liezhao, M. Zhiqiang, Z. Ling, Z. Weijie, L. Jiang, X. Bai, M. Xianglei, L. Biyou, R. Yaozhong, C. Zhaojia and Z. Yuheng, preprint.
20. C. E. Hamrin, Jr., W. D. Arnett, R. J. DeAngelis, X. X. Ding and W. D. Ehmann, *Solid State Commun.*, **69**, 1063 (1989).
21. D. G. Xenikos and T. R. Lemberger, *Rev. Sci. Instrum.*, **60**, 831 (1989).